2-CYANOTETRAHYDROFURANS VIA CYANO-OXYSELENENYLATION

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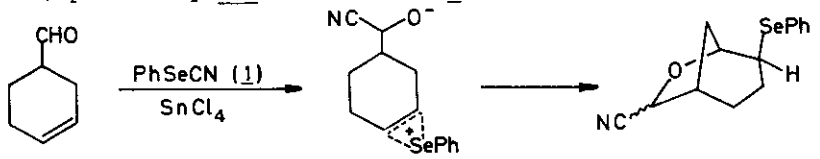
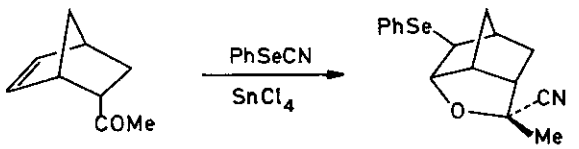
In recent years a number of biologically active natural products possessing tetrahydrofuran moiety have attracted considerable attention. As an extension of our project on organoselenium chemistry using phenyl selenocyanate (1), we wish to report herein a new approach to 2-cyanotetrahydrofurans, which are potentially useful precursors to intermediates of the ionophore antibiotics or other natural products, such as normuscarin.

The new approach is based on the idea that intramolecular C=C and C=O bonds of a γ,δ-unsaturated carbonyl compound could be simultaneously activated by 1 in the presence of $SnCl_4$ as catalyst. Thus treatment of 3-cyclohexene-1-carbaldehyde (2) with equimolar 1 in dichloromethane in the presence of a catalytic amount of $SnCl_4$ afforded a 3:2 mixture of two stereoisomers 4 in 98% yield within 10 min at room temperature, presumably via intermediate 3.



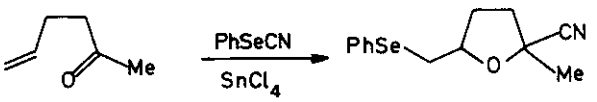
2 3 4

The reaction is also applicable to 5-acetyl-2-norbornene (5), which possesses a ketone group. Surprisingly, 5 gave a single product 6 in 96% yield within 5 min.



5 6

The reaction can be extended also to open-chain enones. Thus 5-hexen-2-one (7) provided 8 as a 3:2 stereoisomer mixture under similar conditions(73% yield).



7 8

Stereoselectivity, versatility and limitations of the reaction will be discussed along with several other examples.